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ON THE CONSTITUTIVE RELATIONS FOR THE HIGH-TEMPERATURE, NONLINEAR EXPANSION OF POLYMERIC COMPOSITES

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ABSTRACT

Constitutive relations are developed for modeling the mechanical response of polymeric materials exposed to high temperatures. These relations are developed from the expression of the first principle of thermodynamics given by Gibbs. These relations are completely general and make no presumptions about the physical size and shape of the material's porosity. As such, these relations are applicable over a wide range of temperatures. Expressions are given for the strain and the entropy of the polymeric composite due to the accumulation of chemical species which result from chemical changes in the resin and for the chemical potentials of each of these chemical species. In addition, the linear relations for porous media can be shown to be a special case of these constitutive relations.

INTRODUCTION

The structural response of polymeric composites subjected to high temperatures is primarily dictated by the chemical changes which occur in the resin constituent. The specific nature of these chemical changes depend upon temperature; resin cure advancement occurs at temperatures below 400°C and molecular depolymerization occurs at higher temperatures. Throughout all temperature ranges, these chemical changes are accompanied by the formation of byproducts and it is the accumulation of these byproducts within the resin, fibers or filler which governs the structural response of these materials. Water is the primary byproduct of the resin curing stage whereas a variety of other byproducts are formed along with water as a result of depolymerization (Sykes, 1967).

To illustrate the effect of chemical changes on the structural response, the results from a series of high-temperature tests conducted on carbon phenolic¹ specimens are shown in Figures 1 and 2 (Hubbert, 1989). In these tests, cylindrical specimens which were 1.0 inches long and 0.25 inches in diameter were heated uniformly and the strain along the cylinder axis was measured as a function of

¹ Carbon phenolic is a laminated, thermosetting polymeric composite made from carbon fabric and is used as thermal insulation in many industries.

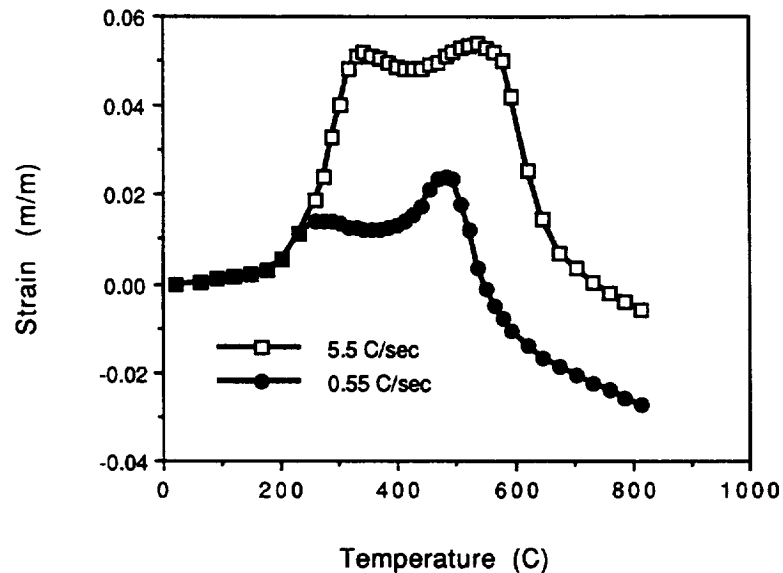


Figure 1. Composite strain as a function of temperature for two different heating rates (Hubbert, 1989).

temperature. The results shown in Figures 1 and 2 are from a particular set of tests where the specimens were fabricated such that the direction which is perpendicular to the fiber plane was aligned along the cylinder axis. Therefore, the results shown are the strain in the material's transverse direction.

These results indicate a highly nonlinear expansion behavior which is due to irreversible processes which occur as the material is heated. These irreversible processes include changes in the chemical state of the material and chemical species migration. A rise in strain with temperature indicates an accumulation of these chemical reaction byproducts in the material whereas a drop in strain indicates a release of energy due to the diffusion of these byproducts.

In Figure 1, the results are shown for specimens heated at two different heating rates to illustrate the effect of heating rate on the expansion response. If the material is heated at a high rate there is less time for the chemical reaction byproducts to diffuse out of the specimens and this in turn produces a higher expansion.

Figure 2 illustrates the effect of moisture content on the expansion response. The expansion results for specimens which were preconditioned in three different environments are compared. Conditioning environment A was 40% relative humidity and 41°C, conditioning environment B was 95% relative humidity and 35°C and conditioning environment C was vacuum dried to a maximum temperature of 100°C to drive out the adsorbed water. As one would expect, the amount of water in the specimens has a significant effect on the expansion. The magnitude of the first peak in the expansion curve which occurs at approximately 300°C is significantly affected by the moisture content of the specimens prior to testing.

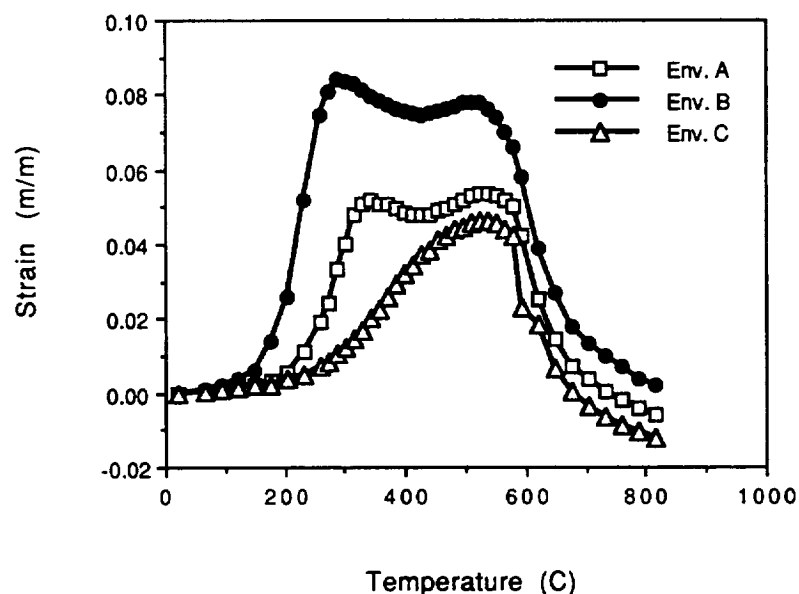


Figure 2. Composite strain as a function of temperature for three different conditioning environments (Hubbert, 1989).

Although Sykes characterized these chemical changes over twenty-five years ago, it has been only recently that analysis methods have become sophisticated enough to address this problem in a rigorous mathematical manner. One of the earliest approaches for modeling these phenomena in polymeric composites was developed by Henderson and Wiecek (1987). Their approach was to treat the byproducts liberated by the chemical reactions as a fluid and to assume that the species migrate through the material like a fluid flows through a porous media. They also assumed that the material remained rigid or incapable of deformation so that the fluid was assumed to flow through a rigid network of pores. Using Darcy's law to model the fluid flow and a mass conservation equation, they determined the fluid pressure in the pores as a function of space and time. This approach was a direct extension of the work of Kung (1972) and Kansa, Perlee and Chaiken (1977) who developed a similar numerical model for wood pyrolysis based upon a similar set of assumptions. These assumptions have a realistic basis in the study of wood pyrolysis since the porosities of wood are quite high (Kansa, Perlee and Chaiken, 1977) particularly after charring has occurred.

More recently, Sullivan and Salamon (1992a) have improved upon this basic approach by incorporating the constitutive relations originally developed by Biot (1941) for poroelastic media into a finite element formulation. This improvement provides the ability to determine the expansion of the material due to internal pore pressure. The results of this method can then be compared directly with the measured response of the material shown in Figures 1 and 2 (Sullivan and Salamon, 1992b).

Within these previous analytical methods, the underlying assumptions are that 1) the byproducts from the chemical changes collectively act like a fluid, 2) there exists a well-defined boundary between the fluid and solid constituents where mechanical equilibrium is maintained and 3) the forces which exist between the solid and fluid constituents are purely of a mechanical nature. However, these assumptions may not be consistent with the physical conditions which are present in polymeric composites as they are heated to high temperatures. For instance, certain carbon fibers used in polymeric composites are known to be hydrophilic (Stokes,

1991) due to activated carbon sites on their surface. The chemical forces between the carbon fibers and water molecules liberated from the resin may become significant in influencing the mechanical behavior of the material. This phenomena could not possibly be accounted for using poroelasticity theory due to the third assumption above.

Another discrepancy which exists between the physical conditions in the polymeric composite and the underlying assumptions of poroelastic media involves the definition of pore volume. The physical size and shape of the pore volume in these materials changes with temperature along with the aforementioned chemical changes. For example, prior to 400°C, the pore volumes are undetectable with a scanning electron microscope at magnifications of 1000x and lower and the pore diameters are smaller than 1 μm (Brown and Clemons, 1992). We could more accurately describe the material's porosity in this temperature range as a free molar volume rather than a physically measurable porosity. The constitutive relations for porous media do not seem relevant for modeling the material response at low and intermediate (100-400°C) temperatures, since if only a few molecules occupy each free molar volume, the concept of a well-defined boundary between the solid and fluid constituents becomes obscured.

As the temperature is increased, the porosity increases with the onset of depolymerization and the formation of cracks. Using helium pycnometry, Brown and Clemons (1992) measured porosities as high as 30% in carbon phenolic specimens heated to 1000°C. The applicability of poroelasticity to carbon phenolic at these higher temperatures is apparent since the microstructure begins to resemble that of granular soils and porous rock and since these are the specific problems which Biot sought to address in developing his original relations.

There are however other constitutive relations for species migration in solids which are not restricted to a specific description of the pore volume. These constitutive relations use the thermodynamic variable known as chemical potential instead of pore pressure as the variable responsible for diffusion phenomena. Gurtin (1977) recognized the equivalence of pore pressure and chemical potential as flow potentials and he appreciated the fact that the chemical potential is the more appropriate of the two variables for problems where the diffusion occurs at a molecular level. We also note the recent work of Weitsman (1990) where chemical potential is used to model moisture diffusion in epoxy resin composites at relatively low temperatures.

Furthermore, the chemical potential is more general than pore pressure. We note the recent work of Gu, Lai and Mow (1992) where the chemical potential is used to model ion diffusion in biological tissues. Their constitutive relations highlight the general nature of the chemical potential as a flow potential since in their relations the chemical potential for water is influenced by both mechanical and chemical phenomena.

The objective of this present study is to establish a unified set of constitutive relations for modeling the structural response of high-temperature, polymeric composites due to the accumulation and subsequent diffusion of chemical species which are liberated from the resin. In the next section, we develop these relations from Gibbs (1906) expression of the first principle of thermodynamics for an open system of variable composition. These relations are completely general and make no presumptions about the physical size and nature of the materials porosity. Also, the forces which are responsible for the diffusion phenomena may be chemical or mechanical in nature. Therefore, these relations are applicable for the analysis of carbon phenolic composites over a wide range of temperatures. These relations express the chemical potentials for each chemical specie which is liberated as well as the composite stress and strain due to the presence of these liberated byproducts.

In the following section, the constitutive relations for poroelastic media are shown to be encompassed by these general constitutive relations since Biot's relations can be derived from thermodynamic principles if certain restrictions are imposed upon the homogeneous mass.

THERMODYNAMICS OF AN OPEN SYSTEM OF VARIABLE COMPOSITION

The Constitutive Relations

An open system is by definition one which is allowed to exchange heat and mass with its surroundings. We consider a homogeneous mass of some arbitrary material and allow heat and mass to cross its boundaries. In the most general sense, this mass may be a solid, a liquid or a vapor. It is composed of the substances $S_1, S_2, S_3, \dots, S_n$ where the proportions of these substances in the mass may vary as heat and masses are added during some thermodynamic process. The term *homogenous* means that the temperature, pressure and chemical composition of the mass are uniform throughout. In other words, no gradients exist in the mass which would cause an irreversible process such as heat or chemical species flow within the boundaries of our mass. As such, we are interested in only equilibrium states and we seek to define the relations between the state variables as the system moves between equilibrium states during thermodynamic processes.

The expression of the first principle given by Gibbs (1906) defines the variation of the internal energy U of this open system as a function of the other state variables. This expression is written as

$$dU = t d\eta - P dv + \mu_1 dn_1 + \mu_2 dn_2 + \dots + \mu_n dn_n \quad (1)$$

where t , P , η and v are the absolute temperature, the hydrostatic pressure, the entropy and the volume of this mass, respectively. Furthermore, $\mu_1, \mu_2, \mu_3, \dots, \mu_n$ denote the chemical potential of the substances $S_1, S_2, S_3, \dots, S_n$, respectively and $n_1, n_2, n_3, \dots, n_n$ denote the number of moles of these n substances in the homogeneous mass. The first term on the right hand side of equation (1) represents the heat added to the mass and the second term represents the work done by the mass during the thermodynamic process. The remaining terms represent the energy added to the system due to the addition of each chemical component.

The state variables of the homogeneous mass are either intensive or extensive quantities. An extensive variable is one whose value depends upon the quantity of material in the thermodynamic system such as volume, entropy or internal energy. An intensive variable is one which is independent of the quantity of material in the system. The intensive variables in equation (1) are pressure, temperature and the chemical potentials. Notice that each term in equation (1) has the form of an intensive variable multiplying the differential of an extensive variable. We further note that the variables t and η are conjugate to one another since they define the thermal state of the homogeneous mass. Likewise, the conjugate variable pairs (P, v) and (μ_k, n_k) define the mechanical state of the homogeneous mass and the Gibbs energy of the k th specie in the homogeneous mass, respectively. Finally, we note that each conjugate pair contains an intensive variable and an extensive variable.

In a homogenous mass with n chemical components only $n+2$ of the state variables are independent. The other state variables are related to the independent variables through certain constraint equations. It is therefore necessary to quantify only $n+2$ of the state variables in order to completely define the thermodynamic state of this homogeneous mass, provided that an appropriate choice has been made for the independent variables. An appropriate choice of independent variables would be to choose one variable from each of the $n+2$ conjugate pairs. For example, we could choose one variable for each chemical component (either μ_k or n_k), one describing the thermal state (either t or η) and one describing the mechanical state (either P or v).

Equation (1) is valid for bodies which are capable of only one mechanical degree of freedom such as inviscid or perfect fluids. However, our problem of interest involves solid bodies where nonhydrostatic stress states are possible. Since, in this case, there are six mechanical degrees of freedom, the number of independent variables is now $n+7$. The mechanical state variables P and v must be replaced with the stress tensor σ_{ij} and strain tensor ϵ_{ij} , respectively and the work term in equation (1) must be replaced with a series of terms where each one represents the work contributed by each of the six independent stress components acting through their associated strain increments. If the stress and strain tensors are defined using a cartesian coordinate system consisting of an x , y and z axis, then equation (1) is written as

$$dU = t d\eta + \sigma_{xx} d\epsilon_{xx} + \sigma_{yy} d\epsilon_{yy} + \dots + \sigma_{xy} d\epsilon_{xy} + \mu_1 dn_1 + \mu_2 dn_2 + \dots + \mu_n dn_n. \quad (2)$$

The sign of the work terms in equation (2) is opposite to that in equation (1) because in equation (1) the pressure was considered positive if it caused a reduction in the volume of the homogeneous mass whereas in equation (2) the stress component is considered positive if it causes an extension of the homogeneous mass.

We choose the variables σ_{ij} , t and n_k as the independent variables and express the remaining variables as functions of these such that

$$\begin{aligned} U &= U(\sigma_{ij}, t, n_k) & \epsilon_{ij} &= \epsilon_{ij}(\sigma_{ij}, t, n_k) \\ \eta &= \eta(\sigma_{ij}, t, n_k) & \mu_k &= \mu_k(\sigma_{ij}, t, n_k). \end{aligned} \quad (3)$$

Using the chain rule of differentiation, the expressions for the differential increments of the state variables ϵ_{ij} , η and μ_k are written as

$$\begin{aligned} d\epsilon_{ij} &= \sum_{r=1}^3 \sum_{s=1}^3 \left(\frac{\partial \epsilon_{ij}}{\partial \sigma_{rs}} \right)_{t, n_L, \sigma_{ij}} d\sigma_{rs} + \left(\frac{\partial \epsilon_{ij}}{\partial t} \right)_{\sigma_{ij}, n_L} dt + \sum_{L=1}^n \left(\frac{\partial \epsilon_{ij}}{\partial n_L} \right)_{t, \sigma_{ij}, n_L} dn_L \\ d\eta &= \sum_{r=1}^3 \sum_{s=1}^3 \left(\frac{\partial \eta}{\partial \sigma_{rs}} \right)_{t, n_L, \sigma_{ij}} d\sigma_{rs} + \left(\frac{\partial \eta}{\partial t} \right)_{\sigma_{ij}, n_L} dt + \sum_{L=1}^n \left(\frac{\partial \eta}{\partial n_L} \right)_{t, \sigma_{ij}, n_L} dn_L \\ d\mu_k &= \sum_{r=1}^3 \sum_{s=1}^3 \left(\frac{\partial \mu_k}{\partial \sigma_{rs}} \right)_{t, n_L, \sigma_{ij}} d\sigma_{rs} + \left(\frac{\partial \mu_k}{\partial t} \right)_{\sigma_{ij}, n_L} dt + \sum_{L=1}^n \left(\frac{\partial \mu_k}{\partial n_L} \right)_{t, \sigma_{ij}, n_L} dn_L \end{aligned} \quad (4)$$

where the stress components σ_{xx} , σ_{yy} , etc. are denoted by σ_{11} , σ_{22} , etc. The subscript n_L denotes differentiation at constant composition and the subscript n_L denotes differentiation with the number of moles of all components held constant except the one in the denominator of the differential. The subscript σ_{ij} denotes differentiation with all stress components held constant and the subscript σ_{ij} denotes differentiation with all stress components held constant except the one in the denominator of the differential.

The constitutive relations given by equations (4) express the differential increments in strain, entropy and chemical potential for each specie during some thermodynamic process in terms of the differential increments of stress, temperature and the number of moles of each specie in the homogeneous mass. These relations are completely general since while deriving them we have made no assumptions about the materials pore structure and no assumptions about the physical state of the chemical species which are added to the mass. The species which enter the homogeneous mass may be in a liquid or a vapor state or these species may enter the homogeneous mass one molecule at a time. The fact that these relations are of a general nature is a direct result of the definition of the chemical potential given by Gibbs which is itself given in very general terms.

In equations (4), the coefficient $\left\{\partial \epsilon_{ij} / \partial \sigma_n\right\}_{t, n_L, \sigma_{ij}}$ is the fourth-order compliance tensor and $\left\{\partial \epsilon_{ij} / \partial t\right\}_{\sigma_{ij}, n_L}$ is the second-order tensor of thermal expansion coefficients. Also, since the change in volume of the homogeneous mass during some thermodynamic process is $dv = d\epsilon_{xx} + d\epsilon_{yy} + d\epsilon_{zz}$, then the partial molar volume for the kth specie is

$$\left\{\frac{\partial v}{\partial n_k}\right\}_{t, \sigma_{ij}, \bar{n}_k} = \left\{\frac{\partial \epsilon_{xx}}{\partial n_k}\right\}_{t, \sigma_{ij}, \bar{n}_k} + \left\{\frac{\partial \epsilon_{yy}}{\partial n_k}\right\}_{t, \sigma_{ij}, \bar{n}_k} + \left\{\frac{\partial \epsilon_{zz}}{\partial n_k}\right\}_{t, \sigma_{ij}, \bar{n}_k}. \quad (5)$$

The coefficient $\left\{\partial \eta / \partial n_k\right\}_{t, \sigma_{ij}, \bar{n}_k}$ is the partial molar entropy of the kth specie.

Finally, we note certain conditions on the coefficients of the constitutive relations given in equations (4) which result from the equality of mixed second partial derivatives of U. The equality of mixed second partial derivatives results from the fact that U is a state function and its differential is an exact differential (Wangsness, 1963). The equality of mixed second partial derivatives of U taken with respect to the independent variables yields

$$\frac{\partial^2 U}{\partial t \partial \sigma_{ij}} = \frac{\partial^2 U}{\partial \sigma_{ij} \partial t} \quad \frac{\partial^2 U}{\partial n_k \partial \sigma_{ij}} = - \frac{\partial^2 U}{\partial \sigma_{ij} \partial n_k} \quad \frac{\partial^2 U}{\partial n_k \partial t} = - \frac{\partial^2 U}{\partial t \partial n_k}. \quad (6)$$

The negative sign in the last two expressions in equation (6) are a result of taking partial derivatives of U with respect to an intensive and an extensive variable. Using equation (2), equations (6) become

$$\begin{aligned} \left\{\frac{\partial \epsilon_{ij}}{\partial t}\right\}_{\sigma_{ij}, n_L} &= \left\{\frac{\partial \eta}{\partial \sigma_{ij}}\right\}_{t, n_L, \sigma_{ij}} & \left\{\frac{\partial \epsilon_{ij}}{\partial n_k}\right\}_{\sigma_{ij}, t, \bar{n}_k} &= - \left\{\frac{\partial \mu_k}{\partial \sigma_{ij}}\right\}_{t, n_k, \sigma_{ij}} \\ \left\{\frac{\partial \eta}{\partial n_k}\right\}_{\sigma_{ij}, t, \bar{n}_k} &= - \left\{\frac{\partial \mu_k}{\partial t}\right\}_{n_k, \sigma_{ij}} \end{aligned} \quad (7)$$

The Chemical Potential

It follows from equation (1) that the chemical potential of the kth specie in the homogeneous mass is

$$\mu_k = \left\{\frac{\partial U}{\partial n_k}\right\}_{\eta, v, \bar{n}_k} \quad (8)$$

where again the subscripts on the bracket indicate differentiation with those variables held constant and the subscript \bar{n}_k denotes differentiation with the number of moles of all components held constant except the one in the denominator of the differential. Furthermore, since the Helmholtz energy function ψ is related to the internal energy by $\psi = U - t\eta$, we can rewrite equation (2) as

$$d\psi = -\eta dt + \sigma_{xx} d\epsilon_{xx} + \sigma_{yy} d\epsilon_{yy} + \dots + \sigma_{xy} d\epsilon_{xy} + \mu_1 dn_1 + \mu_2 dn_2 + \dots + \mu_n dn_n \quad (9)$$

and therefore the chemical potential can also be expressed as

$$\mu_k = \left\{\frac{\partial \psi}{\partial n_k}\right\}_{t, \epsilon_{ij}, \bar{n}_k} \quad (10)$$

where the subscript ϵ_{ij} denotes differentiation with all strain components held constant.

Equation (10) is the mathematical representation of the definition given by Gibbs which states that the chemical potential of any substance in a homogeneous mass is equal to the amount of work required to bring a unit mass of that substance from a state in which its Helmholtz energy is zero into equilibrium with the homogeneous mass in a process where the temperature and volume of the homogeneous mass remain constant². We note that this definition of chemical potential given by Gibbs does not specify the source of the work. This work may be performed by mechanical as well as chemical forces.

CONSTITUTIVE RELATIONS FOR POROUS MEDIA

Biot's Relations for Isothermal Porous Media

Biot (1941) established his constitutive relations for porous media under the pretense that the material is comprised of pores, the fluid constituent must occupy these pores and the solid material is linear elastic. Biot's constitutive relations have been expressed in a number of different forms but perhaps the most useful form was given by Biot and Willis (1957). For materials of general anisotropy under isothermal conditions, these relations are³

$$\begin{aligned}\sigma_{ij} &= C_{ijkl} e_{kl} - \alpha_{ij} p_f \\ \zeta &= \alpha_{ij} e_{ij} + \frac{1}{M} p_f\end{aligned}\tag{11}$$

where σ_{ij} is the total (or overall) stress tensor, e_{ij} is the elastic strain tensor, ζ is the increment in fluid volume and p_f is the fluid pressure in the pores.

The coefficient C_{ijkl} is the fourth-order tensor of elastic constants for the porous solid skeleton. This is sometimes referred to as the drained stiffness tensor since it represents the stiffness due solely to the porous material⁴. The coefficient α_{ij} is a second-order tensor of coefficients which represent the fraction of the pore pressure which contribute to the total stress tensor. These coefficients are a function of the relative stiffness of the porous solid skeleton and the solid material without pores. The coefficient M is a scalar quantity and relates the increments in fluid volume to the pore pressure increments. This coefficient is a function of the porosity, the fluid bulk modulus, the bulk modulus of the solid material and the bulk modulus of the material with pores.

Solving equations (11) for e_{ij} and p_f , we obtain

$$\begin{aligned}e_{ij} &= S_{ijkl}^u \sigma_{kl} + S_{ijkl}^u \alpha_{kl} M \zeta \\ p_f &= -\alpha_{ij} S_{ijkl}^u M \sigma_{kl} + \frac{M}{(1 + \alpha_{ij} \alpha_{kl} S_{ijkl}^u M)} \zeta\end{aligned}\tag{12}$$

where S_{ijkl}^u is the fourth-order tensor of undrained compliances and S_{ijkl} is the fourth-order tensor of drained compliances.

² Note that for isothermal processes the change in the Helmholtz function for the homogeneous mass is equal to the amount of work done on the homogeneous mass.

³ Here and in the following equations, we use the standard practice in tensor notation where repeated indices imply summation and free indices do not.

⁴ The undrained stiffness tensor C_{ijkl}^u , on the other hand, represents the stiffness of the porous material and the additional stiffness from the bulk modulus of the fluid.

For isotropic porous materials, the constitutive coefficients may be determined by four independent tests. These are the *unjacketed compressibility test*, the *jacketed compressibility test*, a test to measure the shear modulus and a test to measure theunjacketed coefficient of fluid content. These tests were described in detail by Biot and Willis (1957).

The Thermodynamic Basis of the Constitutive Relations for Poroelasticity

We can show that Biot's constitutive relations for porous media are encompassed by the general set of relations developed in the previous section. We can derive the general form of the relations given in equations (12) from thermodynamic principles if we consider a homogeneous mass subject to the following restrictions:

- 1) The homogeneous mass under consideration is a porous solid body where the pores are filled with a fluid.
- 2) The substance which is added to the homogeneous mass must reside in the pores of the homogeneous mass.
- 3) The forces which exist between the fluid and solid constituents are purely mechanical.
- 4) All thermodynamic processes occur under isothermal conditions.

The Helmholtz energy for this specific set of conditions was given by Biot (1941) as⁵

$$d\psi = \sigma_{ij} de_{ij} + p_f d\zeta. \quad (13)$$

Since we are interested in only isothermal processes, the conjugate thermal variables t and η are neglected in the expression for the Helmholtz energy given in equation (13).

Following in a similar manner as before, we choose the state variables σ_{ij} and ζ as the independent variables and we can therefore express the differential increments in the variables e_{ij} and p_f as

$$\begin{aligned} de_{ij} &= \left\{ \frac{\partial e_{ij}}{\partial \sigma_{kl}} \right\}_{\zeta} d\sigma_{kl} + \left\{ \frac{\partial e_{ij}}{\partial \zeta} \right\}_{\sigma_{ij}} d\zeta \\ dp_f &= \left\{ \frac{\partial p_f}{\partial \sigma_{ij}} \right\}_{\zeta} d\sigma_{ij} + \left\{ \frac{\partial p_f}{\partial \zeta} \right\}_{\sigma_{ij}} d\zeta. \end{aligned} \quad (14)$$

Equations (12) and (14) are an equivalent set of relations since equations (12) are linear and since both equations (12) and (14) express the strain and pore pressure in terms of the total stress and fluid volume. We note that the derivation of equations (14) was possible only by replacing the conjugate variables μ_k and n_k with the variables p_f and ζ , respectively in the expression for the Helmholtz energy. This substitution is legitimate since pore pressure and chemical potential are both intensive variables describing the energy of a unit quantity of some substance and since the volume increment and the number of moles are both extensive variables

⁵ For linear elastic materials under isothermal conditions, the elastic strain is equal to the total strain, i. e. $e_{ij} = \epsilon_{ij}$.

describing the amount of that substance. Furthermore, the terms μdn and $p_f d\zeta$ describe an increment in energy associated with an incremental quantity of some substance added during some thermodynamic process. We note once again, however, that pore pressure is a quantity which identifies the mechanical force between the fluid and solid constituents whereas chemical potential is more general since it can involve both chemical as well as mechanical forces due to its definition from Gibbs.

Due to the equality of mixed second partial derivatives, the coefficients in the relations of equations (14) are once again subject to the restriction that

$$\left\langle \frac{\partial e_{ij}}{\partial \zeta} \right\rangle_{\sigma_{ij}} = - \left\langle \frac{\partial p_f}{\partial \sigma_{ij}} \right\rangle_{\zeta}, \quad (15)$$

a condition which is satisfied in the relations of equations (12)⁶. Also, since we have replaced the variable n_k with the variable ζ for this specialized homogeneous mass, then it follows that the counterpart to the partial molar volume of the fluid for this special case is

$$\left\langle \frac{\partial v}{\partial \zeta} \right\rangle_{\sigma_{ij}} = \left\langle \frac{\partial e_{xx}}{\partial \zeta} \right\rangle_{\sigma_{ij}} + \left\langle \frac{\partial e_{yy}}{\partial \zeta} \right\rangle_{\sigma_{ij}} + \left\langle \frac{\partial e_{zz}}{\partial \zeta} \right\rangle_{\sigma_{ij}} \quad (16)$$

which, by virtue of equation (12), can be expressed in terms of the poroelasticity coefficients as

$$\left\langle \frac{\partial v}{\partial \zeta} \right\rangle_{\sigma_{ij}} = S_{11ij}^u \alpha_{ij} M + S_{22ij}^u \alpha_{ij} M + S_{33ij}^u \alpha_{ij} M. \quad (17)$$

Finally, we can derive an expression for the chemical potential of the fluid in the porous material for this specific case. Remember that the definition of the chemical potential for some substance in the homogeneous mass was the amount of work required to bring a unit mass of that substance into equilibrium with the homogeneous mass. Under isothermal conditions and within the restrictions of this specialized homogeneous mass, the fluid substance has only one degree of freedom. This lone independent variable is either the fluid pressure or the fluid volume. In order to bring the fluid substance into equilibrium with the fluid-filled porous material, work must be done on the fluid. This work is required to bring the pressure of the fluid from a pressure where the Helmholtz energy of the fluid is zero to the pressure of the fluid in the homogeneous mass. Since there is only one independent variable, the increment in the chemical potential during this process can be expressed as

$$d\mu_f = \left\langle \frac{\partial \mu_f}{\partial p_f} \right\rangle_t dp_f \quad (18)$$

where we have chosen the fluid pressure as the independent variable. We recognize the term in brackets as the partial molar volume of the fluid (Guggenheim, 1933) which, for a condensed phase comprised of a single component, is $1/\rho_f$ where ρ_f is the fluid density. Therefore, equation (18) is written

$$d\mu_f = \frac{dp_f}{\rho_f}. \quad (19)$$

⁶ This condition is satisfied since the undrained compliance tensor is symmetric, i.e. $S_{ijkl}^u = S_{klij}^u$.

Equation (19) is the same as that given by Biot (1972) although Biot arrived at this expression in a different manner. Biot used the concept of a hypothetical reservoir and a strict interpretation of Gibbs definition of the chemical potential. He determined the expressions for the work required to pump a unit mass of the fluid out of the reservoir, compress this fluid to the fluid pressure in the porous material and inject the fluid into the porous material. Integrating his resulting expression by parts, he arrived at equation (19). On the other hand, we have arrived at equation (19) in a more direct manner using thermodynamic identities.

Biot's linear constitutive relations for porous media have been derived from thermodynamic principles and we have thus established the thermodynamic basis for Biot's constitutive relations. Biot realized the role of his relations as a special case of the general set of relations derived from thermodynamic principles (Biot, 1972). Perhaps his motivation for developing his constitutive relations was the fact that the pore pressure is a more tangible quantity than chemical potential since pore pressure can be measured directly. Moreover, the main emphasis behind Biot's efforts was to address problems in the geotechnical field where, in general, these problems involve only mechanical forces between the constituents and the pore volumes tend to be on a larger scale than free molar volumes.

CONCLUSIONS

A set of constitutive relations have been developed for modeling the structural response of polymeric composites subjected to high temperatures. These relations were developed from the first principle of thermodynamics of an open system of variable composition. These relations do not use pore pressure as the flow potential but instead rely on the variable known as chemical potential. These relations are more general since chemical potential is more general than pore pressure and since these relations were developed without being restricted to a specific description of the pore volume. As a result, these relations are applicable over a wide range of temperatures.

The linear constitutive relations for porous media can be viewed as a special case of these relations since the general form of the isothermal relations given by Biot can be derived from thermodynamic principles if the homogeneous mass is restricted to certain conditions. In a future effort, the nonisothermal relations for porous media should also be derived in this manner. This will lead to expressions for the *entropy of mixing* and the *entropy of pressure change* for the porous media in terms of Biot's constitutive coefficients.

In conclusion, it should be noted that these results represent merely the first step in a long and difficult process which will ultimately lead to an accurate and viable analysis method for high-temperature composites. Future tasks will include determination of the constitutive coefficients and verification of this new approach. Determination of the coefficients will involve an extensive effort since these coefficients must be determined through a series of tests conducted on polymeric composite specimens at a number of temperatures and under a variety of test conditions.

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